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SOLIDIFICATION OF GLASS IN MOLDING (A REVIEW)

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A large number of publications addressing the solidification of glass in molding has been systematized. Different aspects of the effect of the basic composition of glass, diathermancy, time and structural factors on solidification processes are discussed. The workability of glasses and the main conditions for mechanized formation of glass articles are considered as well.

The rate of solidification of glass is a critical factor in molding glass articles, which is characterized by viscosity variation with time and can be represented by the following equation:

$$v_s = \frac{d\eta}{dt}\frac{dt}{d\tau},$$

where η is viscosity; t is temperature; and τ is time.

It can be seen that the solidification rate is determined by viscosity variation depending on temperature and temperature variation with time. Viscosity variation depending on temperature, in turn, is related to the chemical composition of glass, whereas temperature variation with time is related to the cooling conditions.

Thus, the rate of solidification of glass depends on the glass composition and the cooling conditions.

Below we will consider factors responsible for the rate of solidification of glass, the working characteristics of glass, and the conditions of mechanized formation of glass articles. Main research trends and results will be discussed. More detailed data on the specified published sources, including the earlier ones, is contained in reviews [1 – 6].

The effect of glass composition on the solidification rate can be split into two directions: the effect of the initial composition and the effect of small colorant additives.

The effect of the main composition of glass on the rate of solidification is caused by the impact of individual oxides on glass viscosity. Numerous studies systematized in publications [2, 3] consider the effect of various oxides on glass viscosity and its measurement methods. The identity of the effect of oxides of the basic glass composition on viscosity and solidification rate is also corroborated by certain special studies. Figure 1 gives generalized viscosity variation curves of "long-term" and "short-term" glasses in solidifying.

The second direction is related to the effect of pigments on absorption in the IR spectrum range, which has an immediate effect on the rate and uniformity of solidification of tinted glasses. In estimating absorption in the IR spectrum range one usually applies the term "diathermancy." This characteristic of glass is essential for the processes of glass melting and formation of glass articles.

Diathermancy of glasses. Systematic research on radiation and absorption in glasses at high temperatures was started by V. M. Dobiash and N. M. Litvinov (1930) and V. Éitel' and V. Lange (1931). The studies of V. Éitel' and V. Lange demonstrated that clear glass has the lowest radiating capacity, whereas colorants introduced into glass to a different extent increase its radiation capacity.

The light transmission of clear and tinted glasses in a temperature range of 2 – 600°C was investigated in the stu-

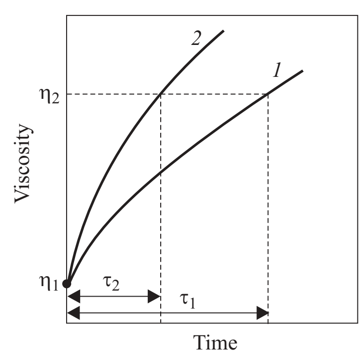

Fig. 1. Solidification of "long-term" (*1*) and "short-term" (*2*) glasses.

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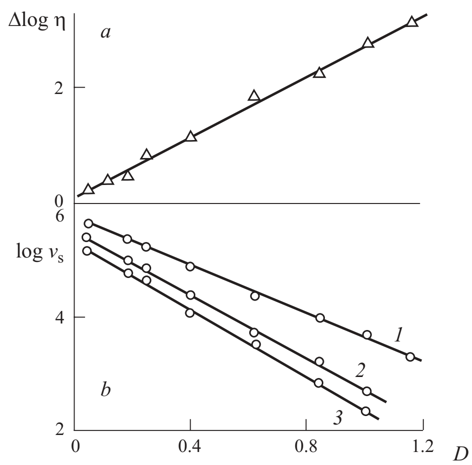

Fig. 2. Dependence of homogeneity η (*a*) and solidification rate v_s (*b*) on optical density of glass *D* in the spectral range of 1.1 μm: *1*, *2*, and *3*) solidification rate at 2, 5, and 10 mm from the surface, respectively.

dies of E. I. Avramenko (1941) and A. Holland and V. Terner (1941). A decrease in light transmission and a shift of its maximum to the long-wave spectrum with increasing temperature was observed. E. I. Avramenko found that chromium- and manganese-bearing glasses have low absorption in the IR range. With an equal concentration of the colorant, the highest absorption is registered in cobalt-bearing glasses, next, copper and iron-bearing glasses. Heat transfer in heated glass was studied by V. V. Rodnikova (1949, 1951). Dependences characterizing the specifics of radiation heat transfer in clear and tinted glasses were obtained.

The absorption properties of glasses in the IR radiation range were studied in detail by L. Gentzel (1951) and N. Neurot (1952). The notion of radiant conductivity was introduced in an analogy to thermal conductivity. The dependence of radiant conductivity on temperature and on the presence of colorant components was established.

The studies of different glasses in a wide temperature interval were continued by F. Grove and M. Jelliman (1955). Some theoretical aspects of heat transfer by radiation in clear and tinted glasses in the industrial conditions were analyzed in studies by R. Gardon (1955, 1961), V. Geffken (1959), S. Kruzhevski (1961), and other researchers.

The results of experiments in IR radiation absorbed by glasses tinted by transition element compounds are summarized in [7]. Data are given on different degrees of oxidation of transition metals depending on temperature. It is demonstrated that absorption in the majority of glasses decreases, whereas absorption in chromium-containing glasses insignificantly increases. A review of experiments performed and some refined data on high-temperature absorption in clear and tinted glasses in the Na – Ca – Si and K – Pb – Si systems is contained in [8]. The results of studying the kinetic factors of the solidification of clear and tinted glasses are given in [9]. The dependence of the uniformity and rate of solidification on the optical density of glasses are given in Fig. 2. It is observed that the level of diathermancy of glasses affecting the solidification process characterizes the forces of interaction of the colorant complexes with the basic silicon-oxygen glass skeleton.

An approximate method for estimating diathermancy based on transmission in the range of 1000 – 1100 nm is applied in [10] to determine the technological parameters of tinted container glasses. This method is successfully implemented in several studies, in particular, estimating reasons for the variation of glass melt diathermancy in an operating tank furnace [11]. A review of the latest studies in diathermancy is given in [12], where the role of diathermancy in the formation of glass containers is illustrated.

Kinetics of glass solidification. Glass melt solidification aspects were studied by a direct practical estimate of the workability of glass and its qualitative characteristic depending on the glass composition. This is facilitated by the accumulation of data on glass viscosity, measurement methods, and data on the dependence of viscosity on the temperature and composition [2, 3].

Studies to a certain extent addressing the rate of solidification of glasses are not numerous. The first studies in this sphere represented an attempt of a qualitative characteristic of viscosity variation rate depending on glass composition, mainly on the presence of colorant oxides.

S. English in 1923 summarized practical experience, refined the results of some earlier studies, and observed that the viscosity variation rate close to the annealing temperature is nearly identical; a differences in the viscosity variation rate for different glass compositions is observed at the temperature of article molding. Comparative qualitative characteristics of temperature and viscosity variations for clear and tinted glasses are contained in works of V. Tsimmerr, S. English, V. Terner, and other researchers (1925 – 1928).

Specialized research on the kinetics of glass solidification was started by S. English and V. Terner (1928), G. Gelhof (1928), and I. I. Kitaigorodskii and N. V. Solomin (1934). These were the first studies that experimentally established a qualitative dependence between the cooling rate, the viscosity variation, and the chromaticity of glass. These studies demonstrated that in drawing filaments of clear and tinted cobalt-bearing glass the clear filament always came out longer than the tinted one. The difference in the length of the filaments increased with increasing concentration of CoO. It was also established than when the glass melt cools in a crucible, tinted glasses have significantly larger temperatures and viscosity gradients across the crucible depth than clear glasses. Based on the increase of this gradient I. I. Kitaigorodskii and N. V. Solomin (1934) ranked the colorant oxides in the following series: MnO_2 – Fe_2O_3 – FeO – CoO. They also recommend estimating the working properties of glass using the time span between the beginning of cooling and the solidification of external layers.

Further progress in research on glass solidification kinetics was based mainly on the methods used by the above scientists.

Summarizing materials based on research methods, the following groups can be pointed out:

– methods based on measuring temperature at various points of glass melt in cooling with subsequent determination of viscosity based on the temperature-viscosity characteristics;

– methods based on determining the geometrical parameters of a molded glass melt portion in the course of cooling;

– methods based on monitoring the structure-sensitive properties of glass.

When using the first group of methods, glass melt was cooled in a crucible, in a mesh, or molded as a sample of a certain shape. For temperature control, thermocouples were inserted into the glass melt at different depths. These were the most common methods in the early study of the kinetics of glass solidification. An original method for cooling glass in a mesh was proposed by O. K. Botvinkin and M. V. Okhotin (1941).

When using methods of the second group, the size of the fibers drawn from mold fillets joined at the ends, the bulb size in vertical drawing of rods, and the deformation parameters of samples were determined. The method of vertical drawing of glass rods is closest to industrial glass-drawing conditions [13].

With the third groups of methods, glass melt was cooled in a crucible and the structure-sensitive property (electric conductivity) directly related to viscosity was monitored [14].

Among the early publications dedicated to the kinetics of glass solidification one should note the integrated research performed by O. K. Botvinkin, M. V. Okhotin, E. I. Avramenko, and T. E. Golba (1941). They investigated the effect of various factors on the solidification process by studying the light transmission of glasses depending on temperature, heat capacity in a wide spectrum range, and the rate of cooling. The results of this research were summarized and their direct relationship to the solidification process was demonstrated.

Extensive research on the viscosity and working parameters of glass, including the solidification rate, was performed by D. Bow and V. Terner (1942 – 1945) who carried out experimental and production studies for a wide range of glass compositions. The cooling and solidification rate control of glasses inside metal molds during the mechanized formation of glass articles was performed in [15, 16]. This line of research is also addressed in reviews [1, 4, 6].

The analysis of some experimental and analytical data on cooling and solidification of glasses is given in [17]. Equations for describing the process of glass solidification and the temperature coefficient of viscosity are obtained.

Structural aspects of solidification. I. V. Borovikov [18] studying cross-sections of molded articles established that a laminar structure arises in glass during forming and subsequent cooling of articles, which is located parallel to the forming surface of the article. In sheet glass this structure has the form of bands rounded off near the edges; in hollow cylindrical articles and in freely formed solid glass tubing it has the form of concentric circumferences. According to measurement data, the thickness of these microlayers is 2 – 4 μm. The laminar structure in tinted glass is more evident than in clear glass. In the opinion of the author, the laminar structure is formed in the abnormal temperature interval of glass.

The structural studies performed by the authors in [19] demonstrated that the presence of a destructive surface layer is regular for any industrial articles. Accordingly, destruction centers become the seeds of structural weakening on which brittle destruction focal points are localized.

Workability of glass. Speaking of the workability of glass, one usually implies a set of physicochemical properties and technological characteristics affecting the formation of articles. A study by T. Adams (1923) is one of the earliest works estimating the workability of glasses.

Considering the temperature dependence of glass viscosity, it should be noted that some researchers used certain points on the curve $\log \eta - t$ to characterize the workability of glass. The calculations of some working characteristics based on indexes are of certain interest for mechanized production of glass articles [20]. Such characteristics include the working interval, the temperature of glass delivered for molding, the relative speed of glass-forming machines, and the crystallization index.

The expression for the working interval index,

$$W = t_S - t_A ,$$

where t_A and t_S are the temperatures corresponding to viscosities of $10^{6.65}$ and $10^{12.4}$ Pa · sec, makes part of all formulas for the calculation of working indexes.

It should be noted that working indexes are not absolute and are indicative only for comparing glasses of significantly different compositions. Examples of analysis of the workability of industrial glasses using working indexes are given in [4, 21 – 26].

The effect of temperature expansion and surface tension on the workability of glasses is considered in the early publications of R. Swain and R. Winks (1927, 1928). These studies attempt to relate the thermal expansion of glasses with their working characteristics. A hypothesis is put forward that glass with higher thermal expansion is more prone to the formation of surface notches. As for surface tension, only a qualitative description of the phenomena related to the surface force effect is given. An attempt at qualitative systematizing of such phenomena is made.

The studies dedicated to the effect of surface tension on the formation process remained scarce. The research on glass fiber headed by M. S. Aslanova (1979) proposed to characterize the capacity for fiber formation based on the ratio of viscosity to surface tension under a certain temperature. However, it should be noted that as temperature varies, the

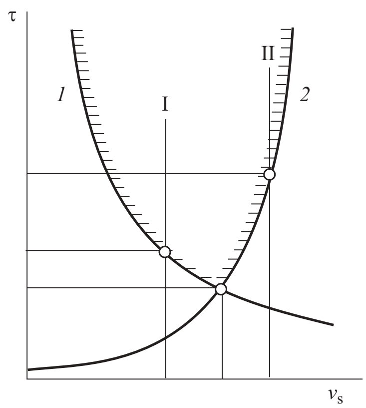

Fig. 3. Possible formation regimes (I and II) for different solidification rates: *1* and *2*) duration of solidification and deformation, respectively.

value of the ratio η/σ depends on the viscosity value, since surface tension depending on temperature varies insignificantly.

The study in [27] analyzes the role of viscosity and surface tension in the formation of glass articles. It is demonstrated that surface tension has no perceptible effect on the formation of most industrial products. Its effect grows as the size of articles or molding object significantly decreases (trimming product surface, formation of glass ribbon edges, edges of glass articles in fusion, free formation of microspheres, beads, and other small articles). In this case surface tension forces significantly exceed gravity and viscous resistance forces.

The factors of the workability of glasses showing the effect of the composition of material components, the glass-melting furnace regime, etc. are described in [28]. A review of research on the working properties of glass and the conditions of mechanical formation of glass articles are give in [4].

Main conditions for mechanized formation of glass articles. The process of formation of glass articles under industrial conditions acquires specific features depending on the type of article and the forming method and includes different technological stages and operations in different order.

However, all forming methods have some common features determined by the physicochemical properties of glass.

The physicochemical and technological characteristics of glasses affecting the molding process have been considered above. The authors in [29] analyze some common regularities of formation. Two processes are combined in forming glass articles: deformation of glass melt and its gradual solidification. They start simultaneously but have different durations. The dependence of the duration of each process on the rate of solidification is inverse: with increasing solidification rate the time of solidification decreases and the duration of deformation grows. The best is a formation schedule in which the total time is the minimally possible.

Figure 3 shows two possible formation schedules. In the first case the deformation time is less than the solidification time and the total formation duration is equal to the solidification time. This is the most typical of industrial practice: a molded article requires a certain time for its solidification. To speed up the production process, the formation duration should be decreased at the expense of raising the solidification rate. In the second case, the deformation duration is longer than the solidification duration and the formation duration is equal to the deformation duration. Such formation regime is not advisable. In this case the formation duration could be decreased by decreasing the solidification rate. The authors in [29] provide approximated relations showing the correlation of the formation duration with various factors: physical properties of glass, geometrical characteristics of articles, and formation conditions.

Numerous studies are dedicated to the conditions of formation of specific products, and they are systematized in [1, 4 – 6, 30]. The most topical are the problems of applying the main technological principles, especially the proportionality principle [30], since compliance with these principles provides an optimum combination of working and service characteristics.

The formation efficiency depends on the glass composition and the cooling conditions. The importance of applying a rational glass composition is corroborated by factory production parameters. For instance, the transition to the aluminomagnesium composition of glass in its time nearly doubled the efficiency of vertical-drawing glass machines. Moreover, the use of this composition raised as well the output of glass-forming machines for glass containers. Furthermore, the application of this composition decreased the crystallization propensity of glass, which decreased losses caused by crystallization defects. Subsequent intensification of the glass-melting process, new molding methods, and new highly efficient glass-forming machines modified the requirements imposed on glass compositions and virtually eliminated the problem of crystallization.

Consequently, modifications of glass compositions are directed to improving glass workability and ensuring necessary service parameters, primarily chemical resistance. Such modifications are related to decreasing the content of Al_2O_3, MgO, and Na_2O in glass and increasing the content of CaO [24]. By decreasing glass melt viscosity at high temperatures CaO intensifies glass melting, and at the formation temperature CaO increases the glass solidification rate, which improves the machine efficiency. A partial replacement of Na_2O by K_2O in mechanized production of glass containers can be recommended as well for a smooth control (increase) of the solidification rate and chemical resistance. As for tinted glasses, in addition to ensuring required protective characteristics, it is advisable to use glasses with higher diathermancy.

One should note as well the importance of the transition to high-calcium compositions in the domestic production of glass containers. Apart from foreign experience [24], a positive domestic experience is seen, for instance, at the Moscow

Electric Lamp Works (MÉLZ) that has achieved a notable improvement in glass melting and forming conditions.

Requirements imposed on the quality of glass and glass articles are getting increasingly stricter. Therefore, the problem of supplying steady-quality raw materials to glass-making factories is topical. Obviously, a constancy of optimum technological parameters will contribute to raising the production efficiency.

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